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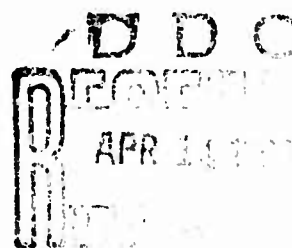
FOREIGN TECHNOLOGY DIVISION



SYNTHESIS OF CERTAIN HOMOLOGS OF ADAMANTANE FROM ADAMANTANE CARBOXYLIC-1 ACID

by

S. Landa, Y. Burkhard, and Y. Weiss



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EDITED TRANSLATION

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By: S. Landa, Y. Burkhard, and Y. Weiss

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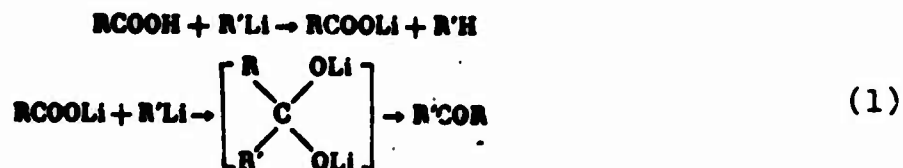
ABSTRACT

The reaction of alkyl lithium with adamantane carboxylic-1 acid is used to synthesize ketones, which are then reduced by the Clemmenson method to produce homologs of adamantane. Also, carbinols obtained as by-products of the initial reactions are reduced by the Clemmensen method to produce a series of hydrocarbons. It is stated that the method outlined in the article gives higher yields of reaction products than previously published procedures. Also, the previously undescribed 1-tret-kutyl adamantane was synthesized. Orig. art. has: 5 formulas and 2 tables.

SYNTHESIS OF CERTAIN HOMOLOGS OF ADAMANTANE FROM ADAMANTANE CARBOXYLIC-1 ACID

S. Landa, Y. Burkhard, and Y. Weiss

The literature contains little information about the synthesis of ketones from free acids and alkyl lithium [1]. It is known that the yield of ketones from the reactions of lower carboxylic acids is low. A higher yield is obtained in the reaction of acids in which the number of carbon atoms is greater than five. We found that adamantane carboxylic-1 acid reacts well with $R'Li$, as is shown on diagram (1):



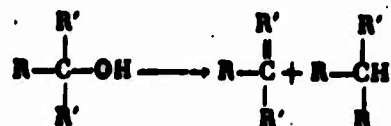
However, in this case besides the desired ketone there is incidental formation of a small quantity of tertiary alcohol [1, 2], especially when a large excess of alkyl lithium is applied (diagram 2):



The reaction mixture was reduced by the Clemmensen method:



During reduction the olefin and corresponding saturated hydrocarbon are formed from the tertiary alcohol produced during the reaction:



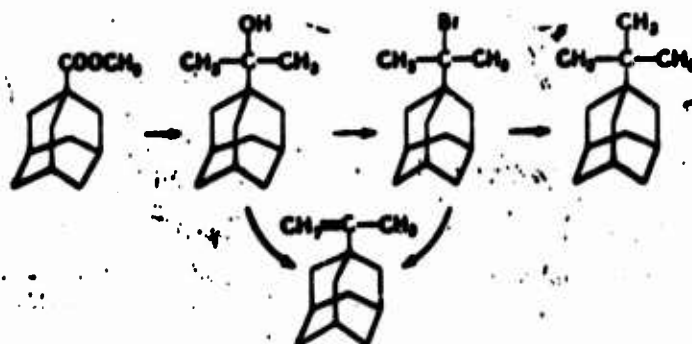
We did not examine the mechanism of formation of these hydrocarbons in detail.

Identification of the by-products of the reaction was conducted by gas-liquid chromatography, by comparison with synthetic standard preparations. Separation of the hydrocarbon mixture was realized with the help of preparative gas-liquid chromatography.

Only the reaction of adamantane carboxyl-1 acid with n-alkyl lithium gives a satisfactory yield; the reaction does not proceed with isopropyl lithium.

The reactions described in this work are suitable in general for syntheses of 1-n-alkyl adamantanes. In contrast to works published earlier [3, 4], the method ensures a higher yield of reaction products.

The following method was used to synthesize tert-butyl adamantane: the reaction of the methyl ester of adamantane carboxylic-1 acid with methyl magnesium iodide yielded 2-(1-adamantyl)-propanol-2, from which the corresponding bromide was synthesized with thionyl bromide; the bromide was then transformed into tert-butyl adamantane during reaction with methyl magnesium iodide. However, the content of this hydrocarbon in the reaction products amounted to only 22%; the remaining 78% was 2-(1-adamantyl)-propene. Since 2-(1-adamantyl)-2-bromopropane introduced into the reaction [chart(5)] was not analyzed, but was only purified of excess thionyl bromide, it is difficult to say whether 2-(1-adamantyl)-propene appears during the synthesis of the bromide or during the reaction of the bromide with methyl magnesium iodide.



(5)

Separation of the reaction mixture was accomplished with the help of preparative gas-liquid chromatography.

Experimental Section

Alkyl lithium was prepared by the usual method [5]. The reaction with adamantane carboxylic-1 acid was conducted in absolute ether in a nitrogen atmosphere at a temperature from -40 to -35°C . Yields of reaction products are given in Table 1. Properties of the synthesized hydrocarbons are shown in Table 2.

Table 1. Yield of reaction products.

Alkyl lithium	Yield of wet ketone, calc. on acid taken, wt. %	Content of tertiary alcohol in wet ketone, mol. %	Unreacted acid, wt. %
CH_3Li	80.3	5.0	15.8
$\text{C}_2\text{H}_5\text{Li}$	36.7	20.0	41.5
$n\text{-C}_3\text{H}_7\text{Li}$	74.8	6.0	9.0
$\text{iso-C}_3\text{H}_7\text{Li}$	—	—	94.4

Table 2. Properties of synthesized hydrocarbons

Hydrocarbon	T _{melt} °C	T _{boil} °C	n _D ²⁰	Calc., %			Found, %	
				C	H		C	H
1-ethyl adamantane	-57.7	218	1.4950	87.73	12.27		87.80	12.22
1-n-propyl adamantane	+7.5	218.2*[6]	1.4950*					
1-n-butyl adamantane	-12.0	234	1.4929	87.56	12.44		87.61	12.47
		253	1.4923	87.43	12.57		87.46	12.51
3-(1-adamantyl)-pentane	not determined	262*[7]	1.4917*					
			1.4998	87.30	12.70		87.41	12.78
3-(1-adamantyl)-pentene-2	not determined		1.5000*[8]					
1-tret-butyl adamantane	111.7-		1.5164	88.16	11.84		88.22	11.87
2-(1-adamntyl)-propene	113.0	-	-	87.43	12.57		87.49	12.53
	not determined		1.5106	88.56	11.44		88.62	11.46
Literature data.			1.5088[9]					

Conclusions

Methyl-(1-adamantyl)-, ethyl-(1-adamantyl)-, and n-propyl-(1-adamantyl)-ketones were synthesized by the reaction of adamantane carboxylic-1 acid with alkyl lithium; by reduction of these products by the Clemmensen method the following hydrocarbons were obtained: 1-ethyl adamantane, 1-n-propyl adamantane, and 1-n-butyl adamantane.

The following carbinols were formed as by-products of the reaction of adamantane carboxylic-1 acid with alkyl lithium: 2-(1-adamantyl)-propanol-2, 3-(1-adamantyl)-pentanol-3, and 4-(1-adamantyl)-heptanol-4. Their reduction by the Clemmensen method will yield 2-(1-adamantyl)-propene and 2-(1-adamantyl)-propane, 3-(1-adamantyl)-pentene-2 and 3-(1-adamantyl)-pentane, 4-(1-adamantyl)-heptene-3, and 4-(1-adamantyl)-heptane. These hydrocarbons were identified with the help of gas-liquid chromatography, by comparison with synthesized standard preparations. Besides this, 3-(1-adamantyl)-pentene-2 and 3-(1-adamantyl)-pentane were separated by means of preparative gas-liquid chromatography.

As compared to procedures published earlier, this method gives higher yields of the reaction products.

In the work we also synthesized the previously undescribed 1-tret-butyl adamantane, formed together with 2-(1-adamantyl)-propene.

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